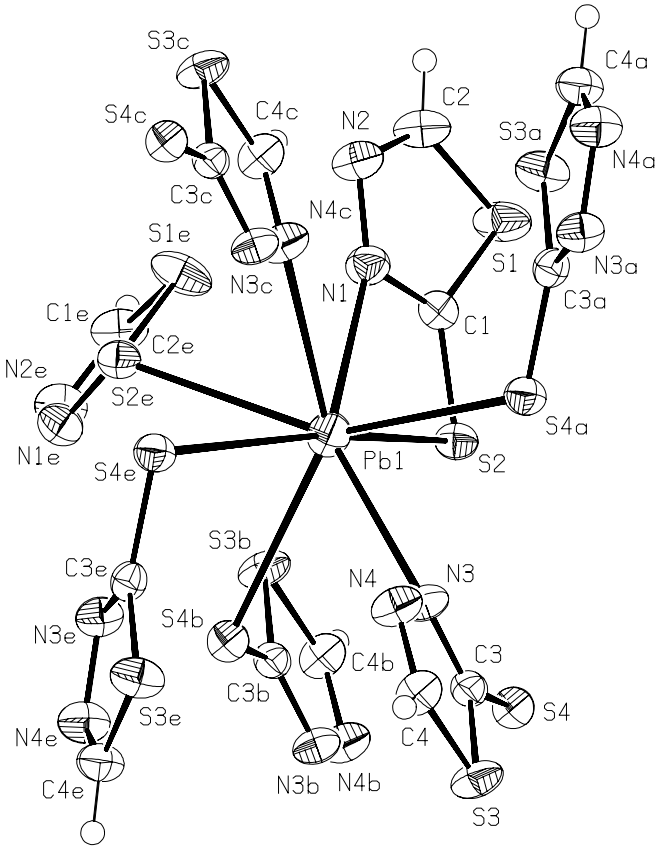
Crystal structure of poly-bis(1,3,4-thiadiazolium-2-thiolato)lead(II), $Pb(C_2HN_2S_2)_2$

Jian-Hua Qin*, Pu-Zhou Hu, Jian-Ge Wang and Bang-Tun Zhao

Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang, Henan 471022, P. R. China

Received September 22, 2007, accepted and available on-line November 30, 2007; CCDC no. 1267/2190



Abstract

$C_4H_2N_4PbS_4$, orthorhombic, *Pbca* (no. 61), a = 9.2513(6) Å, b = 8.4347(5) Å, c = 24.105(2) Å, V = 1881.0 Å^3, Z = 8, $R_{gt}(F)$ = 0.015, $wR_{ref}(F^2)$ = 0.036, T = 291 K.

Source of material

The mixture of $Pb(NO_3)_2$ (1 mmol) and 1,3,4-thiadiazolium-2-thiolate (2 mmol) was stirred into 15 mL aqueous solution at room temperature. Then the pH was adjusted to 3 with dilute hydrochloric acid. The reaction mixture was then heated on a water bath for 5 h at 50 °C, and then filtered. Colorless crystals were separated from the mother liquor by slow evaporation at room temperature after 2 weeks.

Discussion

Over recent years, the control of heavy-metal lead in industrial effluents is of crucial importance for environmental reasons. One of the scientific most important features concerning high performance for lead removal is the coordination behavior of Pb ion [1-3]. Furthermore, thiadiazoles have attracted increasing attention because of their potential applications in coordination and polymer chemistry [4-6]. Recently, we synthesized a versatile bifunctional ligand based on 1,3,4-thiadiazole [7].

The crystal structure of the title compound consists of polymeric units of the $[Pb(C_2HN_2S_2)_2]$ moieties. Each Pb(II) ion is linked by two N atoms and three S atoms from four different 1,3,4-thiadiazolium-2-thiolate molecules, and the Pb—N and Pb—S bond lengths are 2.695(2) Å (d(Pb—N3)), 2.754(2) Å, (d(Pb—N1)) and 2.8586(7) Å (d(Pb—S2), 2.9824(7) Å (d(Pb—S4a), 3.0759(7) Å (d(Pb—S2c), respectively, being in the normal range observed for other complexes containing S or N donors [8-9]. Each Pb atom is in an eight-coordinated environment with the five mentioned bonds and three weaker Pb—N and Pb—S bonds with the distances d(Pb—S4b) = 3.3552(7) Å, d(Pb—S4c) = 3.3557(7) Å, d(Pb—N4d) = 3.046(2) Å) (symmetry codes: (a) –1/2+x,3/2–y,1–z; (b) 1–x,1–y,1–z; (c) 1/2–x,–1/2+y,z; (d) –x,1–y,1–z). The thiadiazole ligands act as chelating-bridging, which results in a two-dimensional framework parallel (001). The thiadiazole rings are planar with maximum deviations from the ring planes of 0.004(2) Å for N3 atom and 0.048(1) Å for S2 atom.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.03 × 0.13 × 0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	187.79 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II CCD, φ/ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10458, 2151
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1987
$N(param)_{refined}$:	118
Programs:	SHELXS-97 [10], SHELXL-97 [11], SHELXTL [12]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	8c	0.0311	0.6553	0.2174	0.045
H(4)	8c	0.1521	0.5694	0.6604	0.040

* Correspondence author (e-mail: jh_q128105@126.com)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb(1)	8*c*	0.15911(1)	0.47309(1)	0.445781(5)	0.04174(7)	0.03474(7)	0.02308(7)	–0.00491(4)	0.00369(4)	0.00110(4)
S(1)	8*c*	0.22571(8)	0.7518(1)	0.27001(3)	0.0366(4)	0.0621(5)	0.0300(4)	–0.0126(3)	–0.0052(3)	0.0186(3)
S(2)	8*c*	0.35936(6)	0.65714(8)	0.38246(3)	0.0261(3)	0.0333(3)	0.0242(3)	0.0001(2)	–0.0009(2)	0.0018(3)
S(3)	8*c*	0.37955(7)	0.66264(9)	0.63280(3)	0.0334(3)	0.0509(4)	0.0216(4)	–0.0112(3)	–0.0034(3)	–0.0017(3)
S(4)	8*c*	0.53253(7)	0.71500(8)	0.52203(3)	0.0297(3)	0.0315(3)	0.0271(4)	–0.0017(2)	0.0023(3)	0.0005(3)
N(1)	8*c*	0.1183(3)	0.5479(3)	0.3357(1)	0.033(1)	0.036(1)	0.028(1)	–0.0040(9)	–0.002(1)	0.003(1)
N(2)	8*c*	0.0319(2)	0.5453(3)	0.2888(1)	0.032(1)	0.048(1)	0.031(1)	–0.006(1)	–0.005(1)	–0.001(1)
N(3)	8*c*	0.2636(2)	0.6024(3)	0.53981(9)	0.028(1)	0.041(1)	0.022(1)	–0.0027(9)	–0.0025(9)	–0.005(1)
N(4)	8*c*	0.1615(2)	0.5646(3)	0.5797(1)	0.029(1)	0.048(1)	0.030(1)	–0.0071(9)	–0.0016(9)	–0.004(1)
C(1)	8*c*	0.2282(3)	0.6468(3)	0.3320(1)	0.026(1)	0.028(1)	0.022(1)	0.0022(9)	0.003(1)	0.001(1)
C(2)	8*c*	0.0766(3)	0.6438(4)	0.2516(1)	0.028(1)	0.058(2)	0.027(2)	–0.000(1)	–0.003(1)	0.000(1)
C(3)	8*c*	0.3849(3)	0.6569(3)	0.5612(1)	0.027(1)	0.024(1)	0.025(1)	0.003(1)	–0.002(1)	–0.0006(9)
C(4)	8*c*	0.2078(3)	0.5896(3)	0.6291(1)	0.033(1)	0.039(1)	0.028(2)	–0.007(1)	0.004(1)	–0.002(1)

Acknowledgment. This work was supported by the Natural Science Foundation of Henan Province (grant nos. 2004601012, 0511020100), which is gratefully acknowledged.

References

1. Porter, Y.; Halasyamani, P.S.: Syntheses, Structures, and Characterization of New Lead(II)-Tellurium(IV)-Oxide Halides: $Pb_3Te_2O_6X_2$ and $Pb_3TeO_4X_2$ (*X* = Cl or Br). Inorg. Chem. **42** (2003) 205-209.
2. Ying, S. M.; Mao, J. G.: Novel Layered Lead(II) Aminodiphosphonates with Carboxylate-Sulfonate and 1,3,5-Benzenetricarboxylate Ligands as Pendant Groups or Intercalated Species. Eur. J. Inorg. Chem. **6** (2004) 1270-1276.
3. Anderson, R. J.; di Targiani, R. C.; Hancock, R. D.; Stern, C. L.; Goldberg, D. P.; Godwin, H. A.: Characterization of the First N_2S(alkylthiolate)lead Compound: A Model for Three-Coordinate Lead in Biological Systems. Inorg. Chem. **45** (2006) 6574-6576.
4. Coyanis, E. M.; Boese, R.; Autino, J. C.; Romano, R. M.; Della Veďova, C. O.: Synthesis, spectroscopic, theoretical and structural studies of new trihalomethyl sulphenyl derivatives of 5-methyl-1,3,4-thiadiazole-2-thiol. J. Phys. Org. Chem. **16** (2003) 1-8.
5. Crane, J. D.; Emeleus, L. C.; Harrison, D.; Nilsson, P. A.: A non-symmetrical compartmental ligand derived from acetazolamide and its mononuclear cobalt(III) complex with an empty outer compartment. Inorg. Chim. Acta **357** (2004) 3407-3412.
6. Zhang, Y.; Li, J. R.; Du, M.; Zou, R. Q.; Bu, X. H.: Novel Silver(I) Coordination Polymers with a Series of Bis(arylthio)ether Ligands Bearing a *trans*-2-Butene Backbone. Cryst. Growth Des. **5** (2005) 215-222.
7. Wang, L.; Zhang, J.; Ye, B. X.; Hu, P. Z.; Zhao, B. T.: 2,2′-(1,4-Butanediyldithio)bis(1,3,4-thiadiazole). Acta Crystallogr. E**62** (2006) o4844-o4846.
8. Mahjoub, A. R.; Morsali, A.: Syntheses and characterization of lead(II) salts with 4,4′-bithiazole ligand: X-ray crystal structures of $[(BTZ)_2Pb(NO_3)_2]$ and $[(BTZ)Pb(SCN)_2]_n$ (a new polymeric compound). Polyhedron **21** (2002) 197-203.
9. Evans, R. N.; Mihalcik, D. J.; Jones, D. S.; Rabinovich, D.: *cis*-Dichlorotetrakis(2-mercapto-1-*tert*-butylimidazole)lead(II). Acta Crystallogr. E**59** (2003) m370-m372.
10. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
11. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
12. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 5.10. Bruker AXS, Madison, Wisconsin, USA 1998.